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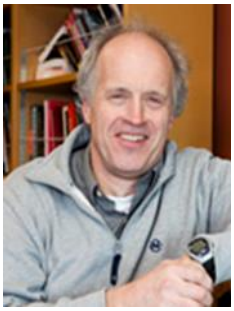
THE EFFECT OF USING LIDS IN DIFFERENTIAL SCANNING CALORIMETER EXPERIMENTS FOR DETERMINING THE HEAT OF REACTION OF WOOD



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ABSTRACT
An analytical method based on the theory and experimental techniques of differential scanning calorimeter is proposed to investigate the determination of the heat of reaction for wood in experiments with and without crucible lids. It is found that the heat exchange dynamics are different for the two cases during decomposition which causes the rate of energy transfer to differ and the values of heat of reaction to vary quantitatively. However, these results still demonstrate consistent energy absorbing and releasing behaviour during the decomposition process in both lid scenarios. In addition, the quantitative differences for the heat of reaction only have a weak effect on the predictions of burning behaviour for cone calorimeter simulations in Fire Dynamics Simulator.

Keywords: wood pyrolysis, heat of reaction, crucible lids, DSC

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1. INTRODUCTION

The heat of reaction for wood is an important parameter to describe the changes in energy during its thermal decomposition process. Differential scanning calorimeter (DSC) is a technique which has been widely used to determine the heat of reaction by measuring the energy differences between a crucible containing a sample of the material and an empty reference crucible. However, there is no specific guidance on whether the crucibles in experiments involving the decomposition of wood should be closed with lids or open without lids. In Rath et al's [1] study, different DSC results for wood were obtained from the experiments with and without lids. It was considered that the differences in emissivity between the formed char and the reference crucible caused an extra radiation effect in the experiments without lids. However, by taking out the radiation effect, the results for the heat of reaction for the experiments without lids were still inconsistent with the results with lids. It is questionable whether the formed char only affects the scenarios without lids, whether the radiation is the only factor causing the difference in the results, and whether the difference will cause significant influence on the application of the DSC results in other analyses.

In order to resolve these problems, a method combining mathematical expressions applicable to the theory of DSC and experimental analysis techniques is proposed in this work to quantitatively determine the differences in the heat of reaction of wood in the experiments with and without lids. In addition, an investigation is carried out to evaluate the influence on the predictions of burning behaviour by applying the different heats of reaction obtained from the DSC to Fire Dynamics Simulator, version 6.1.0 (FDS6) [2] simulations of the cone calorimeter. The work described in this paper is a component of a larger study investigating the dynamics of fires in tunnels with forced ventilation.

2. METHOD FOR ANALYSING HEAT OF REACTION

The DSC technique involves the measurement of the difference in heat flow rate dq_S/dt between a sample crucible and an empty reference crucible while they are heated at a constant rate within a controlled environment [3]. During the decomposition of virgin wood in nitrogen it is expected that the sample generates gaseous products, a remaining solid product and that a residue is leftover at the end of the process. When thermal lag is negligible, the heat flux is [3]:

$$dq_S / dt = dh_S / dt + (C_{SS} + C_{SC} - C_{RC}) dT / dt \quad (1)$$

where dh_S/dt is the kinetic heat flow rate produced by transformations and reactions of the sample; C_{ss} and C_{sc} denote the heat capacity of the sample and the heat capacity of the crucible on the sample side, while C_{rc} denotes the heat capacity for the crucible on the

reference side, and dT/dt is the heating rate. In order to calculate the heat of reaction for a charring material such as wood based on dh_s/dt, three DSC runs are required to extract the kinetic heat flow from dq_s/dt, which are: an empty crucible run, a virgin sample run and a residue run. These runs are used to assess the influence of the empty crucible on the heat flow rate, to exclude the heat capacity of the virgin sample and to examine the heat flow rate of the residue respectively. According to Equation 1, the measured total heat flow rate for an empty crucible run is:

$$dq_b / dt = (C_{sc} - C_{rc})dT / dt \tag{2}$$

When using Equation 1 to subtract Equation 2, the heat flow rate without the thermal effect of the empty crucible is obtained such that:

$$dq_S / dt - dq_b / dt = dh_S / dt + C_{ss}dT / dt \tag{3}$$

In Equation 3, C_{ss} combines the heat capacity of the virgin sample ($m_{vs}(t)c_{p(vs)}$) and the heat capacity of the solid product ($m_{sp}(t)c_{p(sp)}$) generated during the decomposition. Similarly, dh_s/dt also consists of the kinetic heat flow rate for the virgin sample (dh_{vs}/dt) and for the solid product (dh_{sp}/dt). Therefore, Equation 3 can be expanded as:

$$dq_S / dt - dq_b / dt = dh_{vs} / dt + (m_{vs}(t)c_{p(vs)})dT / dt + dh_{sp} / dt + (m_{sp}(t)c_{p(sp)})dT / dt \tag{4}$$

where $c_{p(vs)}$ and $c_{p(sp)}$ refer to the specific heat of the virgin sample and solid product; $m_{vs}(t)$ and $m_{sp}(t)$ are the mass for the virgin sample and solid product at time t. The term $dh_{sp}/dt + (m_{sp}(t)cp_{(sp)})dT/dt$ represents the heat flow rate for the solid product generated during the run. The exact value of this term can be obtained through an extra run for the residue remaining from the sample run, the heat flow rate for this extra run without the thermal effect of the crucible is expressed as:

$$dq_{re} / dt - dq_b / dt = dh_{re} / dt + (m_{re}c_{p(re)})dT / dt \tag{5}$$

where dq_{re}/dt denotes the measured heat flow rate for the residue; dh_{re}/dt and m_{re} refer to the kinetic heat flow rate and the mass for the remaining residue. When the dimensionless product conversion fraction $\alpha = (m_0 - m_{(t)}) / (m_0 - m_{re})$ is defined, where m_0 is the initial sample mass, $m(t)$ is the mass measured during the decomposition at time t, the relationship between the heat flow rate of the solid product in the sample run and Equation 5 can be written as: $\alpha(dq_{re}/dt - dq_b/dt) \approx dh_{sp}/dt + (m_{sp}(t)c_{p(sp)})dT/dt$, Therefore, the kinetic heat flow rate of the virgin sample based on the three experiments can be written as Equation 6, where a positive value is for an endothermic reaction and a negative value is for an exothermic reaction.

$$dh_{vg}/dt = (dq_S/dt - dq_b/dt) - \alpha(dq_{re}/dt - dq_b/dt) - m_{vs}(t)c_{p(vs)}dT/dt \quad (6)$$

3. EXPERIMENTAL PROCEDURE

Wood samples are selected from the same material that has been used as the fuel load in a large-scale tunnel testing programme [4]. A TA Instruments SDT Q600 thermal analyser is employed for the experiments. Two series of experiments using two 90 μL aluminium crucibles (~5 mm in diameter), with and without lids, are carried out. To ensure the repeatability of all experimental data, three sets of experiments under identical conditions are conducted for the series with lids, and the series without lids. All experiments are conducted at a heating rate of 5 K/min in a pure nitrogen environment by flowing nitrogen gas at 100 ml/min into the furnace. Samples are evenly placed within the crucible and the mass of the samples in each experiment are controlled at ~10 mg. Each run starts from ambient temperature heating up to 873 K. The furnace is cooled down to ambient temperature in a nitrogen gas environment at the end of each run to prevent any residue remaining in the crucibles being oxidized.

4. RESULTS AND DISCUSSIONS

4.1 Results of TGA-DSC

The decomposition rate (DTG) curves and the mass loss curves are shown in Figure 1a and Figure 1b for runs with and without lids. As shown in Figure 1a, three major reaction regions can be identified for both scenarios: the hemicellulose reaction region, from the initial increase of decomposition rate (~400 K) to the shoulder part (~575 K); the cellulose reaction region, which is mainly for the range of the peak of the curve and the lignin reaction region, from the sharp decay in the rate after the peak (~640 K) to the wide long tail part (~850 K) [5]. However, the decomposition rates behave slightly differently based on the DTG curves for the two scenarios. Figure 1b also shows that less residue remains when the lids are not used. The differences in the two figures are possibly due to the different heat exchange mechanisms caused by the presence and absence of lids.

Figure 2a and Figure 2b illustrate the heat flow rates for the empty crucible, sample and residue runs with and without lids. The heat flow rate curves recorded from the empty crucible runs determine the baselines for the sample and residue runs, as explained in Equation 3 and Equation 5. The results from the heat flow rate from the residue runs and from the empty crucible runs almost overlap between 400 K and 600 K, indicating the heat flow rate generated from the residue is negligible within this range.

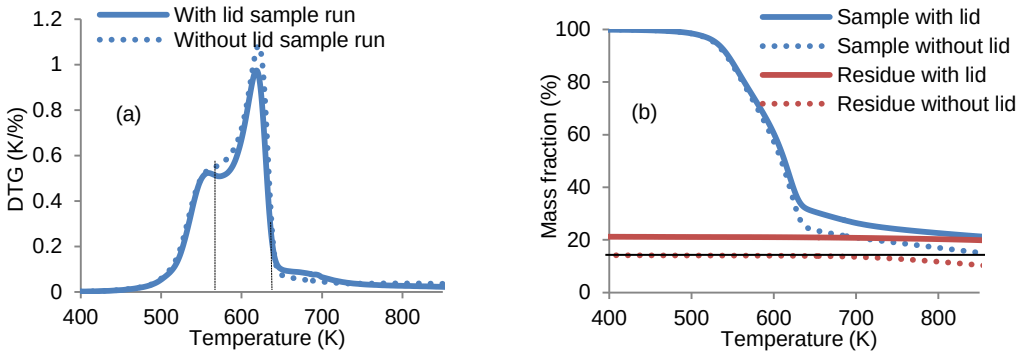

Figure 1 TG curves: (a) DTG curves for wood; (b) Mass loss curves for wood and residues.

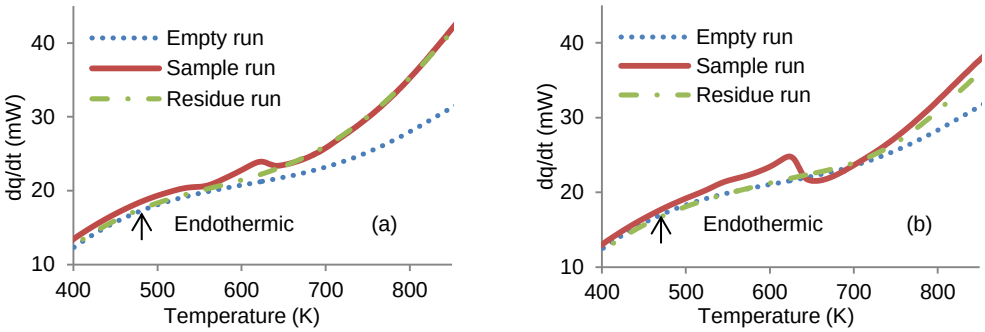

Figure 2 DSC experimental curves: (a) with lids; (b) without lids.

However, at the high temperature range, i.e. above ~720 K, the heat flow rate curve for the residue run overlays the sample run when lids are used (Figure 2a). This means the heat flow rate for the sample run, recorded at high temperatures, is mainly determined by the heat capacity of the residue. For the scenario without lids, the heat flow rate curve for the residue run is slightly lower than the curve for the sample run at the high temperature range, which suggests further reactions or transformations may have occurred during the residue run. The reduction in mass from ~720 K onwards for the residue run without lids (Figure 1b) also reflects the residues have possibly undergone reactions at this high temperature range. However, the formed residue is not expected to have any further decomposition in a pure nitrogen environment. Therefore, it is reasonable to assume that samples are fully decomposed during the sample run in this study. Based on this, the heat flow rate curve for the sample run in Figure 2b is manually shifted to overlap heat flow rate curve for the residue run at a temperature of ~720 K onwards.

4.2 Heat flow rate for virgin samples

Equation 6 is applied to extract the kinetic heat flow rate for the decomposition of virgin wood, where an equation for the specific heat of dry wood is used to determine the heat capacity of the virgin sample: $c_{p(vs)}$ = 3.867(T + 273.15) +103 [6] and the $m_{vs}(t)$ is defined as: (1-α)$m_{0.}$ Figures 3a and 3b show the kinetic heat flow rate of the virgin sample for runs with and without lids along with the corresponding DTG curves for a better interpretation of the thermal decomposition process.

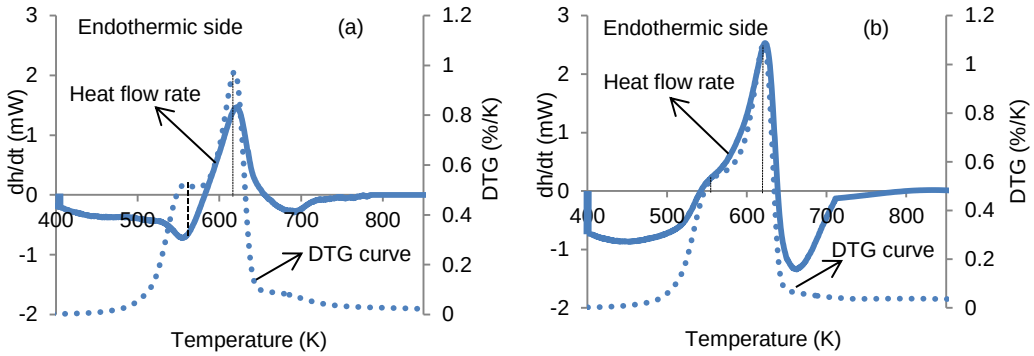

Figure 3 Heat flow rate & DTG curves: (a) with lids; (b) without lids.

There is no obvious change of decomposition rate on DTG curves at the temperature range from 400 K to 450 K, suggesting no apparent gas or solid product is generated. However, exothermic behaviour is indicated on the heat flow rate curves in both lid scenarios at this temperature range, which suggests exothermic reactions have still occurred without obviously changing the mass of the samples. Yang et al. [7] found that some complex functional groups (such as C=O, C=C) are rich in the hemicellulose and lignin components of wood. Hence, the exothermic reactions are possibly the result of the breaking down of the double bonds of these functional groups without causing any obvious change in mass.

In the scenario with lids (Figure 3a), concave upward and downward peaks (at ~555 K and 620 K, respectively) on the heat flow curve correspond to the regions for hemicellulose and cellulose, suggesting hemicellulose decomposes exothermically, while the decomposition of cellulose is endothermic. However, in the scenario without lids (Figure 3b), there is no clear concave upward peak in the region dominated by hemicellulose, while a pronounced concave downward peak can still be found on the heat flow rate curve for the cellulose region. This illustrates that the decomposition of cellulose is still dominated by an endothermic reaction even though no lid is present. However, it is difficult to conclude that the reaction in the hemicellulose region still

behaves exothermically in this scenario. Rath et al. [2] also observed similar reaction behaviours in their DSC experiments.

The possible reason for the differences in these two scenarios could be attributed to the different decomposition mechanisms occurring during the reactions. As explained in the literature [8], there are two competitive reactions during wood decomposition: the exothermic charring reaction and the endothermic volatile reaction. Hence, in the hemicellulose and cellulose reaction regions, when no lid is used, the generated volatiles are efficiently diffused into the nitrogen environment and heat is efficiently exchanged with the heated environment. Due to the supplement of heat from the environment, the reaction is then pushed toward the endothermic volatilisations which have an opposite cooling effect to balance the heat gained from the environment. Therefore the global heat flow behaviour moves extensively toward the endothermic side, as indicated in Figure 3b. On the contrary, the presence of a lid keeps the generated volatiles within the crucible which may slow down the reaction rate due to the cooling effect from volatile reactions: this results in the decomposition moving toward the charring reaction which is an exothermic reaction generating more heat to compensate for the loss of heat due to the cooling effect.

The third concave peak (at ~680 K) followed by a noticeable rising trend shown on the heat flow curve in Figure 3a corresponds to the lignin decomposition region. A similar correspondence is also found in Figure 3b at ~650 K. The upward concave curve on the exothermic side in these scenarios indicates the decomposition of lignin is dominated by an exothermic charring reaction. When lids are used, the heat generated from the charring reaction is kept within the crucible, which speeds up the decomposition rate and the overall reaction gradually moves toward the volatile reaction side to balance the heat. However, when no lid is used, the generated heat from the charring reaction is efficiently diffused into the nitrogen environment, thus less heat remains within the crucible compared with the scenario leaving lids on. Therefore, for the case without the use of lids, the charring reaction still dominates the overall reaction until sufficient heat is gained from the heated nitrogen environment to accelerate the volatile reaction. Therefore, a much larger concave upward curve is obtained on the exothermic side in Figure 3a than in Figure 3b.

4.3 Heats of reaction and FDS6 simulations

Heat of reaction is defined as the energy required for pyrolysis per unit mass of reactants in FDS6 [2], this definition can be mathematically written as:

$$\Delta h_r = \frac{1}{m_r}\left(\int_{T_{start}}^{T_{end}} \left(\frac{dh_{vg}}{dT}\right)dT\right) * \frac{1}{dT/dt} \tag{7}$$

where m_r is the mass of reactants within the temperature range of a reaction and T_{start} and T_{end} denote the initial and the final temperature for the reaction. The term within the parentheses in Equation 7 is determined by integrating the heat flow curve within the reaction temperature range and the last term dT/dt is the heating rate (5 K/min). In order to estimate the mass of reactants from each reaction region, heat flow curves and the corresponding mass curves for runs with and without lids are plotted in Figure 4a and Figure 4b.

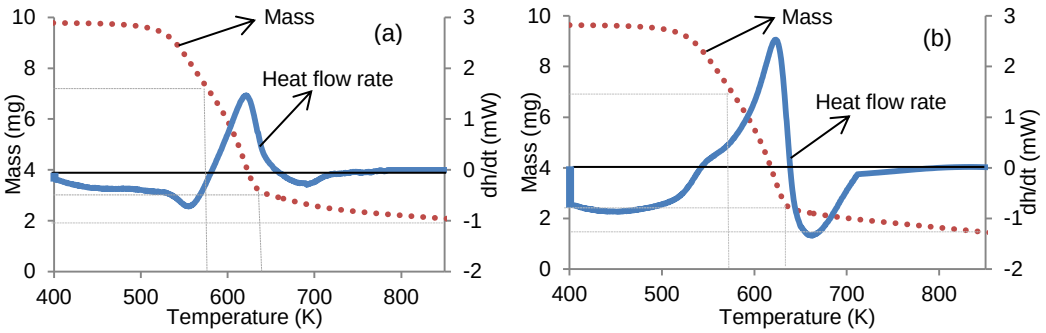

Figure 4 Derivation of heat of reaction: (a) with lids; (b) without lids.

The changes in mass for reactants within each reaction region and the final heat of reaction results for the cases in Figure 4a and 4b are listed in Table 1 as L1 and NL1. In addition, the heats of reaction for other sets of experiments are calculated and listed in Table 1, where Δh_{rh}, Δh_{rc}, and Δh_{rl} are the heat of reaction for the reaction regions of hemicellulose, cellulose and lignin.

The calculated results clarify the decomposition of cellulose is endothermic and the decomposition for hemicellulose and lignin is exothermic in both lid scenarios. These findings agree with the analysis of Yang et al. [7]. However, the differences in results are significant from experiment to experiment, which are possibly due to the experimental variability. Nevertheless, the values still quantitatively indicate some general phenomena: more energy is absorbed or generated in each decomposition region in the absence of lids than in the presence of lids. This is due to the improved heat exchange with the environment in the absence of lids pushes reactions toward the side of endothermic or exothermic reaction to balance the heat in the decomposition.

From a practical point of view, it is worth observing whether the differences in heats of reaction obtained for the different lid scenarios will cause significant differences in heat release rate (HRR) prediction through FDS6, where heat of reaction is used to describe energy changes caused by chemical reactions in the heat transfer equation.

Table 1 Results for heat of reaction

Items		Hemicellulose region			Cellulose region			Lignin region			Total
		$\int(dh_{vg}/dT)dT$ (mW·K)	m_r (mg)	Δh_{rh} (J/g)	$\int(dh_{vg}/dT)dT$ (mW·K))	m_r (mg)	Δh_{rc} (J/g)	$\int(dh_{vg}/dT)dT$ (mW·K))	m_r (mg)	Δh_{rl} (J/g)	Δh_r (J/g)
With lids	L1	-72	3.24	-273	49	5.27	111	-12	1.30	-114	-44
	L2	-65	3.47	-223	33	5.88	68	-56	1.48	-456	-97
	L3	-104	3.08	-405	48	5.13	113	-21	1.26	-199	-97
With-out lids	NL1	-93	3.05	-366	92	5.43	204	-69	1.09	-759	-87
	NL2	-110	3.17	-418	61	5.52	133	-92	1.09	-1017	-174
	NL3	-117	3.22	-438	54	5.32	122	-79	1.15	-828	-177

A cone calorimeter experiment at 35 kW/m^2 incident heat flux is simulated in FDS6 based on different heat of reaction inputs from Table 1, while all other parameters are kept the same. The cone calorimeter data comes from experiments on the same wood material that has been used in the tunnel testing programme [4] previously mentioned. The comparisons of predicted HRR curves with the experimental curve are shown in Figure 5a and Figure 5b.

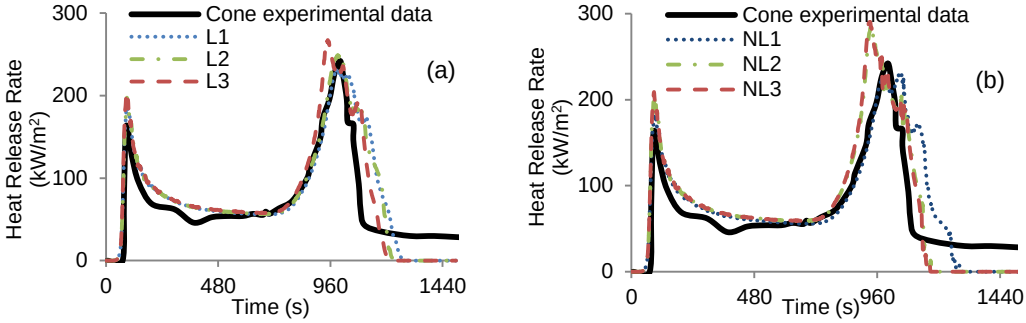

Figure 5 HRR using Δh_r : (a) with lid; (b) without lid.

The predicted HRR curves in the scenarios with lids fit to the experimental data slightly better than the scenario without lid, which indicates the differences of heat of reaction caused by the absence and presence of lids only have a weak effect on the prediction of HRR. Mathematically

the contribution of the energy from the chemical reactions to the overall heat transfer is minor compared to the energy gained from front surface based on the equation of heat transfer in FDS6. Therefore the quantitative differences in the heat of reaction in this study, due to equipment uncertainties or experimental conditions, are still within an acceptable range and do not significantly affect the heat release rate predictions in FDS6.

5. CONCLUSIONS

This study presents an analytical method to investigate the influence of using lids in DSC experiments. The experiments with lids and without lids result in different heat exchange dynamics which lead to differences in the absorption and release of energy during the decomposition of wood. The values of heats of reaction obtained with and without lids differ from experiment to experiment. However, these values still quantitatively indicate more energy is gained and released in the scenario without lids than with lids and these values also have a qualitative consistency in revealing the endothermic and exothermic reaction behaviour in the decomposition process. The predictions of HRR for cone calorimeter simulations in FDS6 are only slightly affected by the differences of heat of reaction in the experimental methods, suggesting the variations of the heat of reaction in this study are within an acceptable range in the application of the pyrolysis model in FDS6.

6. REFERENCES

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